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An Alternative Method of Synthesizing Iron-based Amorphous Alloys

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XRD Technique: A way to disseminate structural changes in iron-based amorphous Materials*.

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Abstract

Prevention of corrosion is a vital goal for the Department of Defense when billions of dollars are spent every year. Corrosion resistant materials have applications in all sort of military vehicles, and more importantly in naval vessels and submarines which come in contact with the seawater. It is known that corrosion resistance property can be improved by the used of structurally designed materials in the amorphous state where the atoms are arranged in a non-periodic fashion and specific atoms, tailored to the required properties can be interjected into the matrix for specific application. The XRD techniques reported here is to demonstrate the optimal conditions for characterization of these materials. The samples, which normally contain different compositions of Fe, Cr, B, Mo, Y, Mn, Si and W, are in the form of powders, ribbons and coatings. These results will be compared for the different forms of the sample which appears to correlate to the cooling rate during sample processing. In most cases, the materials are amorphous or amorphous with very small amount of crystallinity. In the ribbon samples for different compositions we observed that the materials are essentially amorphous. In most cases, starting from an amorphous powder sample, the coatings are also observed to be amorphous with a small amount of iron oxide on the surface, probably due to exposure to air.

Introduction

Prevention of corrosion is a major cost and effort for all sort of metal-based components. This is particularly important when these components are exposed or in contact to harsh environments, for example, water and sea water, acid, gases as well as abrasions. It has been known that chemical corrosion resistance can be improved by the used of structurally designed amorphous materials [1]. Corrosions in periodic condition are attributed to both the atomic structures as well as the microstructures. In the atomic structures, periodic tunnels exist whereby pathways occur where possibly ionic oxygen, nitrogen and hydrogen can travel through a crystal without significant obstructions. Loosely packed grain boundaries and often voids exist in crystalline materials which are susceptible to chemical attacks into the bulk of the materials, thus resulting in poor physical properties. Also, in crystalline structures, there exist anisotropic thermal expansions in the bulk by the nature of the periodic atomic arrangements and thus upon thermal cycling, the microstructures can be changed, resulting in possibly additional grain boundaries, dislocations and voids, which can initiate stress corrosion cracking.

In amorphous materials, also known as metallic glasses, atomic arrangements are essentially almost random where the precise atomic locations are not so critical, thermal expansion can now be highly isotropic, grain boundaries can be eliminated and as well as the presence of periodic tunnels. These behaviors essentially reduced stress corrosion cracking, thus increases the corrosion resistant property. Even though, local chemical short range order does occur in the amorphous arrangement but not in the long range order. Another advantage of using amorphous materials is that it can also be elementally tailored to specific application. Metallic glasses also often exhibit extraordinary mechanical and thermal properties, magnetic behavior and high corrosion resistance. These novel materials could be very important in the future of commercial and defense industries.

Fe-based amorphous alloys are of considerable interest mainly because it is cheaper than non Fe-based materials, say Ni-based alloy C-22. Several Fe-based alloys have been investigated and showed to have good corrosion resistance, for example thermal spray coating of Fe-10Cr-10-Mo-(C,B) by Kishitake et al. [2]; bulk Fe-Cr-Mo-C-B [3]; and Fe-Cr-Mo-C-B-P [4]. Nickel-based amorphous metals have also been developed which exhibit exceptional corrosion performance in acidic environments [5]. Typically, Fe-based alloys are materials which are made up of Iron (Fe), Chromium (Cr), Manganese (Mn), Tungsten (W), Molybdenum (Mo), Boron (B), Yttrium (Y) and many more, and the major component is Fe. These materials are extremely hard which resulted in resistance to abrasion and gouges from backfill operations. Already, Fe-based alloys have been used in enormous number of applications, for example in all kinds of sea vessel, containers, tools and many more. The major problem in these alloys is in corrosion. By convention, specific property can be improved by changing the elemental compositions of these alloys. For example, for corrosion resistance, one probably increases the concentration of Cr, Mo and W, and a few other items at much smaller concentration because of processing considerations, neutron container application, an increase in B and Mo is desired.

One of the critical requirements in the formation of amorphous materials is the high cooling rate needed to capture the atomic arrangements set at from melt. This process will be difficult when the material is forced to cool slowly and hence, allowing the formation of energy crystalline structures. Both Alloy C-22 and Type 316L stainless were found not to be amorphous when prepared as coating under the same conditions for SAM2X5 and SAM1651. As such, it is more practical that the application of amorphous materials to be used for corrosion resistant in the form of thin layer of coating on Fe-based surfaces. Other technique, like sintering large quantity of amorphous materials at temperature below the melting points to build physical vessels or containers is probably not practical.

Several compositions of these Fe-based alloys have prepared and optimize for specific processing conditions and applications by the group at Lawrence Livermore National Laboratory [6]. SAM1651 ($\text{Fe}_{48.0}\text{Cr}_{15.0}\text{Mo}_{14.0}\text{B}_{6.0}\text{C}_{15.0}\text{Y}_{2.0}$) is designed to have low critical cooling rate for processing aid whereas the yttrium-free SAM2X5 ($\text{Fe}_{49.7}\text{Cr}_{17.7}\text{Mn}_{1.9}\text{Mo}_{7.4}\text{W}_{1.6}\text{B}_{15.2}\text{C}_{3.8}\text{Si}_{2.4}$) has a higher critical cooling rate. However,

SAM1651 has higher melt viscosity which made processing more difficult. SAM1651 has also significant boron (B) content, which has a good neutron absorber and can be used for criticality control in baskets for the nuclear waste technology. Other neutron absorbers like gadolinium (Gd) and cadmium (Cd) can also be investigated. Borated stainless steel and Gd-doped Ni-Cr-Mo alloys are being developed for neutron absorption capability, there are issues relating to availability, cost, corrosion and mechanical properties.

Several steps were needed during processing from the manufacturing of the amorphous powder to the coating and during each step the material experience some level of stress and heating. Melt spun samples were also prepared in order to understand the effects of coating process and merely composition differences behavior. To ensure that the materials are indeed amorphous with the appropriate microstructures, x-ray characterization is needed along each step. Experimental x-ray characterization technique has been developed to optimize the investigation of these materials at each step of the processing conditions. This work is part of the effort here at LLNL by the HPCRM team to develop high corrosion resistance materials and hence material developments and processing parameters will be covered by Farmer et. al. [6]. Amorphous powder materials of different compositions are first prepared and then high energy sprayed coated onto parts in order to harvest the corrosion resistant property. Applications of interest are for the use as the skin of submarines and military vessels exposing to sea water or vessels for nuclear waste storage containers.

This paper reports on the characterization effort for the amorphous materials using x-ray diffraction technique. Some brief theoretical background is given in order to interpret the results, instrumentation will also be described and results be provided. The paper also focuses on the technique used to optimize scattering signal for the Fe-based amorphous materials.

Theoretical considerations

The basic theory of x-ray diffraction has been quite well covered in many text books [7]. For crystalline diffraction, specific x-ray peaks can be observed from a diffraction pattern acquired from x-ray diffractometer for crystalline materials. These peaks are the results of constructive interference of the probing x-ray wave. If the sample is single crystal, these peaks have specific arrangements and orientations. The positions and intensities of these peaks are related to the atomic arrangements in the unit cell of the crystals. In general, specific compounds have specific lattice parameters and the compounds can be identified by these parameters.

In an amorphous material, the atoms are not arranged in a periodic fashion such that crystals can be formed. The scattering intensity is then the summation of each individual atom. The time average scattering of non-interacting scattering like mono-atomic gases, the scattering is given by the Debye equation,

$$I_{eu} = \sum_m \sum_n f_m f_n \frac{\sin kr_{mn}}{kr_{mn}} \quad (1)$$

f_m, f_n are the scattering factors, r_{mn} are the inter-atomic distances and k . This equation can be further reduced and converted to an integral,

$$I_{eu} = Nf^2 \left[1 + \int 4\pi\rho(r) \frac{\sin kr}{kr} dr \right] \quad (2)$$

Using algebraic manipulation and defining $\rho(r) = [\rho(r) - \rho_o] + \rho_o$, this equation becomes

$$k[i(k)] = 4\pi \int_0^\infty r[\rho(r) - \rho_o] \sin kr dr \quad (3)$$

where $i(k) = \frac{I_{eu} / N - f^2}{f^2}$, for simplicity and by using the theorem of Fourier's conversion, we can write the radial distribution function as

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_o + \frac{2r}{\pi} \int_0^\infty k[i(k)] \sin kr dk \quad (4)$$

The above expression provided a mean of converting the intensity function, which is in k space ($k=4\pi\sin(\theta)/\lambda$) to the radial distribution function in real space. In this formulation, the atoms are arranged in random fashion with no particular order. There are broad diffraction peaks, which belong to the amorphous structure. The amorphous state does have structure as defined by the radial distribution function and the partial radial distribution, if it is a multiple elements system [8]. For the present effort, such an analysis is not necessary at the moment. In all, the degree of crystalline is correlated to the intensity of each scattering component.

Experimental setups

The X-ray diffraction experiment is carried out using the Philip vertical goniometer in the para-focusing or also known as the Bragg-Bretano method. It is self-focusing and that is the distance between the x-ray focal point to the sample position is equal to the distance between the sample position and the receiving slit for the reflection mode. Thus, the intensity and resolution are optimized and taking advantage of the divergence nature of the x-ray source. Parallel vertical slits are often added to improve the signal to noise ratio. In general, in most diffractometers, scintillation detectors are used. However, the energy resolution is no sufficient to discriminate fluorescence x-rays of certain elements with energy close to the probing x-ray energy. Hence, very often, an analyzing crystal is used after the receiving slit. This is also critical in samples where there are a lot of

fluorescence lines that are close to the characteristic lines, for example for all iron based materials using copper K α radiation. It is also quite common that filtered x-ray source, particularly using Ni foil, which enhances the copper K α radiation intensity, are used, instead of using a diffracted beam monochromator. However, in this case for Fe-based alloy, this technique will not work. The choice of the crystal is based on the crystal mosaic, for energy selectivity and the efficiency. The most widely use energy discriminator is usually graphite for efficiency without significantly scarifying x-ray intensity. This is particularly important for the HPCRM because of the iron content in the samples. Iron fluorescence K α has energy which is close to that of the probing copper K α x-ray.

In the present setup, Copper K α is used with a graphite analyzing crystal. Step scan is performed from 20 to 80° (2 θ) with step size of 0.02° at 4-10 seconds per point, depending on the amount of sample. The generator is maintained at 40 KeV and 30 mA. The samples are loaded onto low background quartz holders. This is because the expected intensity is very low.

Samples

The samples reported and discussed in this paper focuses on SAM2X5 which has the atomic of (50Fe-18Cr-15B-4C-5Mo-2Si-2Mn-2W) and SAM7 (50Fe-18Cr-15B-4C-7Mo-2Si-2Mn-2W). Other compositions are also prepared in this laboratory [6]. The powder samples are manufactured by the atomization technology based on cooling down of extremely small particles in a chamber.

Results and discussion

Figure 1 shows the resulting diffraction pattern for the five SAM2X5 powder samples (A), (B), (C), (D) and (E) manufactured by a commercial company in 2004 (lot #4) and 2005 (lot #5). The differences in these powders are the manufacturing conditions which resulted in differences in particle sizes as indicated in the plot. They are also resulted from different buckets. Clearly, crystalline can be observed on top of the amorphous component for samples (A)-(D). In sample (E), the powder is essentially amorphous and sample (D) shows a small amount of crystallinity. The crystalline lines in Figure 1 can then be indexed using the data base from ICDD (International Center for Diffraction Data) which conclude that the crystalline materials resulted from the process are alloys of boron chromium, chromium carbide, possibly iron chromium and iron. Hence, these results provide information which will help in changing the processing parameters in order to avoid the formation of crystallinity.

Figure 2 shows the x-ray diffraction spectra for the melt-spun ribbons for SAM2X5 and its variants, (a) SAM2X1, (b) SAM2X3, (c) SAM2X5 and (d) SAM2X7 for the Mo series where (a) is 1%, (b) 3%, (c) 5% and (d) 7% Mo concentration. The results clearly indicate that these ribbon samples are amorphous as evidence by a single broad x-ray peak. Although, not shown here, the melt spun ribbon for 316L (57Ni-22Cr-13Mo-2Fe-3W-Co) alloy and C22 (Fe-20Cr-10Ni-3Mo-Mn) alloy did not result in an amorphous structure.

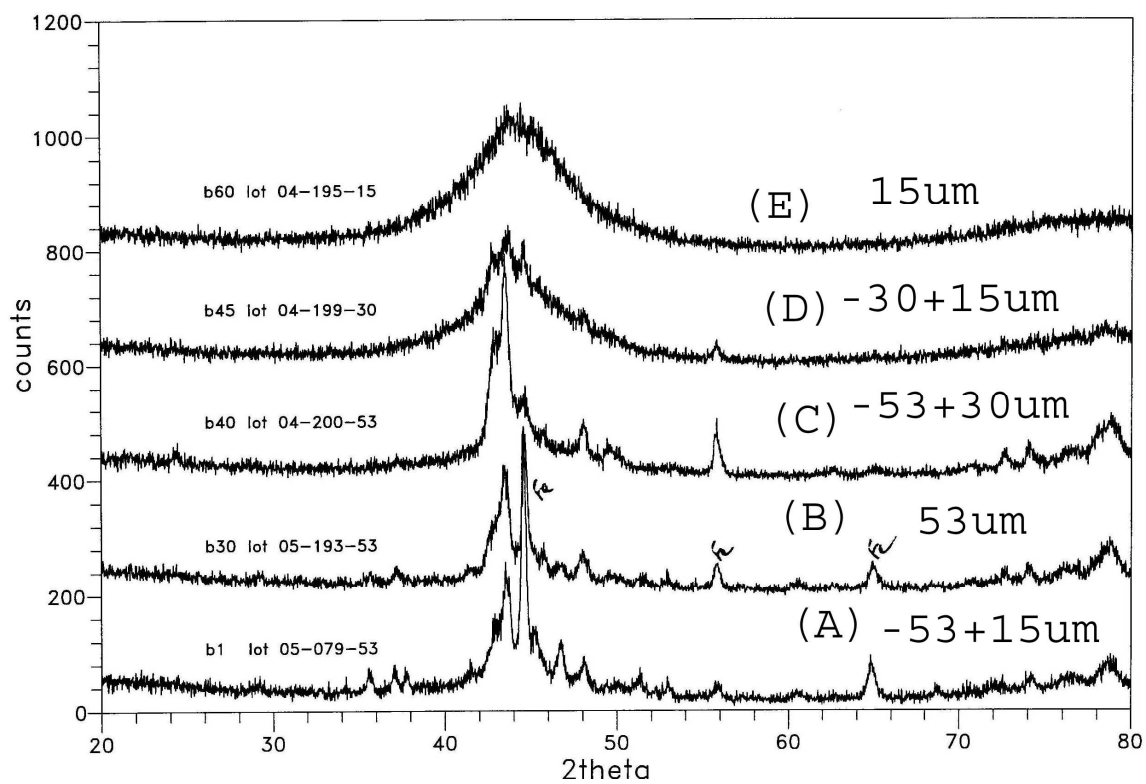


Figure 1: XRD diffraction patterns of SAM2X5 powders taken from different buckets

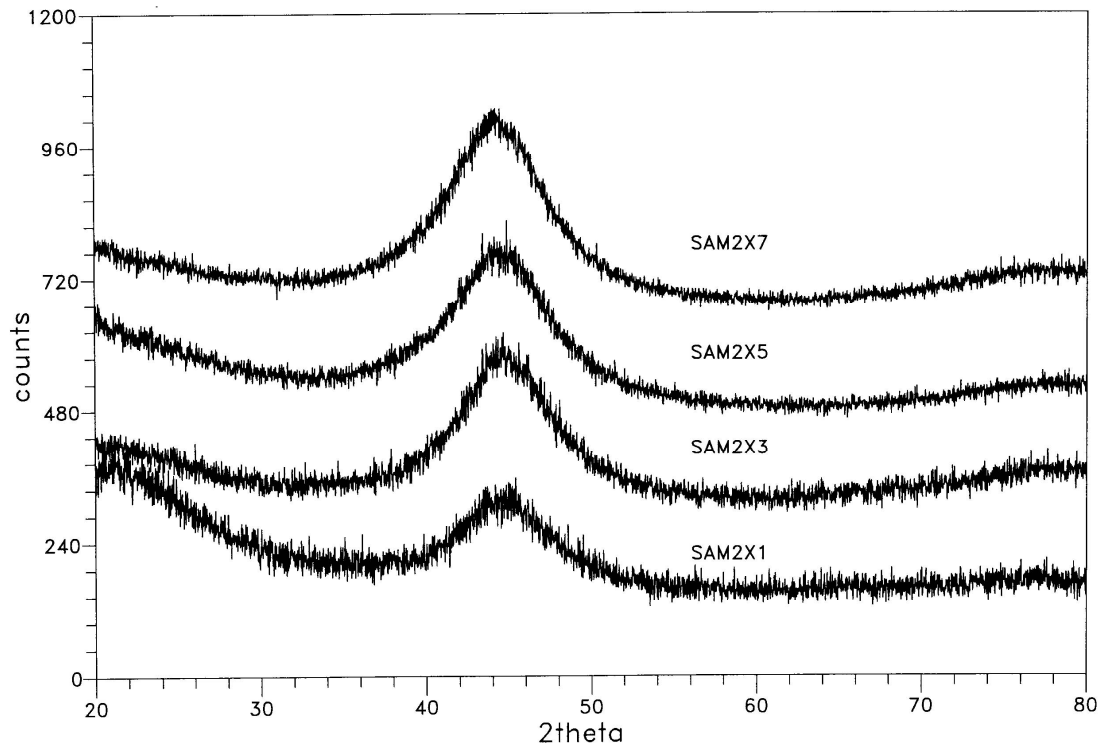


Figure 2: XRD diffraction patterns for SAM2X5 and slight variants.

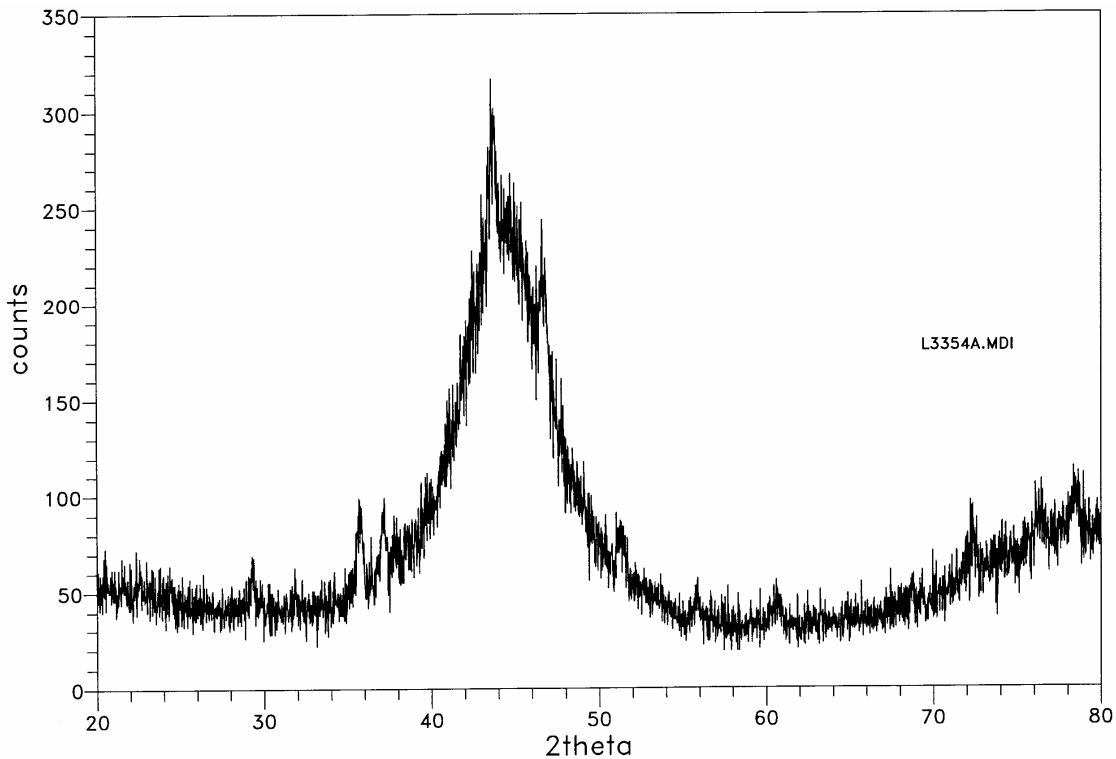


Figure 3: XRD diffraction pattern of a SAM2X5 coating on 316L substrate

Figure 3 shows the result for SAM2X5 coating on 316L stainless steel. The powders are deposited using the HVOF (high velocity oxy-fuel) technique, which involves a combustion flame, a gas gun with particle velocity equal to 3-4 times the speed of sound. The amorphous alloys clearly experienced some level of heat and stress, some level of crystallinity is observed which is tentatively identified as bcc ferrite and chromium boron compound. These crystalline components can be identified and processing parameters can be adjusted to avoid crystalline formation. Since then, amorphous coating of SAM2X5 has been achieved.

Discussions and Conclusion

X-ray diffraction technique has been developed to examine the structure of SAM samples in the form of powder, ribbons and coatings. Since the samples contain a significant amount of iron hence, diffracted beam discrimination is needed. The results suggest that the production of amorphous iron-based alloys is critically dependent on the multiple elemental compositions. C22 and 316L alloys did not form the amorphous phase. Differences in crystallinity can be observed from samples to samples. The crystalline components are due to selected components of the alloy, for example, boron chromium, chromium carbide, iron chromium, iron carbide and boron iron. This information is used to redefine the processing conditions hence the present powders being investigated are essentially amorphous.

Amorphous melt-spun ribbon samples cannot be prepared for C22 and 316L materials,

they both show crystallinity. All the ribbons samples exhibit an amorphous structure. There are some differences in the structure of the thermal spray coatings depending on the starting powder samples. In most cases, the major amorphous component can be observed with a small amount of crystalline component. However, starting from an amorphous powder, an amorphous coating can be achieved with a small amount of crystallinity due to oxidation of iron.

The present work clearly indicates that XRD technique can be used to disseminate structural changes in iron-based amorphous materials, thereby provide information on the state of the material during each step of the fabrication. Information on the surface and bulk formation can also be gotten.

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